N.D.
U.

ohexane are carried out
ıs PAH.

nded Soxhlet-extraction
dred gram aliquots of wet
nts with ^{14}C-BaP or
nd were Soxhlet-extracted
acetone extract were

:ly analyzed by liquid
from gross amounts of
ssitated a simple purifica-
column (3.5 x 1.1 cm o.d.
recovery measurements.
ıtitatively recover both
ely extended to 72 hours.

onstant weight to allow
analytical results in terms
of sediment for PAH
ıH are reduced by this

next isolated by a two-step
. complex isolation pro-
rior to adsorption column
isolate suitable for analysis
of water are concentrated
nl burette and are eluted
will be used throughout).
liluted to 60 ml with water,
These cyclohexane ex-
ts described above.

concentrated to 10 ml and
sture) alumina, using a
1 (300 ml). The PAH
acers: a diaromatic fraction
and acenaphthalenes and
H and their alkyl derivatives.
ne by evaporative concen-
sure and temperature.

H fractions is achieved by
with those of authentic
on a 6.6 m x 3 mm o.d. glass
h Supelcoport. Tempera-
ows elution of PAH ranging
. coronene) in approximately

Difficult-to-resolve PAH isomers which are separated with fairly good success include phenanthrene/anthracene, benz[a] anthracene/chrysene, and benzo[e]-pyrene/benzo[a] pyrene.

PAH concentrations are calculated by comparing GC peak areas with those of an external standard. Recovery corrections for losses of PAH in isolation and handling are estimated by liquid scintillation counting 0.1 volume aliquots of the fractions in 10 ml of scintillator solution prepared by dissolving 15 g of 2,5-diphenyloxazole and 190 mg of 1,4-bis[5-phenyloxazole] benzene in 1 gal of reagent grade toluene.

FLUORESCENT SPOT TEST FOR PNA DETECTION

The information in this section is based on:

> *Evaluation of Sensitized Fluorescence for Polynuclear Aromatic Hydrocarbon Detection,* EPA Report 600/7-79-207, August 1979, prepared by T.R. Smith of TRW Defense and Space Systems Group for the U.S. Environmental Protection Agency.

The original fluorescence spot test was developed by Arthur D. Little, Inc. (53) under contract to the EPA and is based on the phenomenon of sensitized fluorescence. The objective of the effort of T.R. Smith was to determine if the test could be used as a screening aid for samples submitted for PAH analysis by gas chromatography/mass spectrometry (GC/MS). The procedure can potentially provide a low cost screening technique to predetermine the presence of PAH.

Spot Test Procedure

No preparation of the sample is required. The sample should be in a solution to allow easy application to the test substrate. Solids and gases can be analyzed with some modification of the application technique (53).

A Chromatovue ultraviolet cabinet (Model C-70) was used to expose the samples. The 254 nm lamp source was used. A 7.0 cm circular ashless Whatman No. 42 filter was used as the support for the samples. The sensitizer used was naphthalene at a concentration of 60 μg/μl in methylene chloride.

The spot test is carried out as follows:

(1) Draw three circles in pencil on a piece of Whatman No. 42 filter paper as close to one another as feasible.

(2) Using a 10 μl syringe, spot the filter paper with the sensitizer (naphthalene). 1 μl of sensitizer should be spotted on the leftmost circle and 1 μl of sensitizer should be spotted on the center circle. The spots should not be allowed to overlap. The substrate should be supported so as not to touch any surface.

(3) Allow the solvent to evaporate from the filter paper.

(4) 1 μl of sample is then applied to the rightmost and center circles. Again, allow the solvent to evaporate and do not allow the substrate to touch any surface until the solvent has evaporated.

(5) The filter paper is placed in the Chromatovue cabinet.

(6) Compare the spots visually with the unaided eye.

(7) If the center spot (sample plus sensitizer) fluoresces brighter than the sensitizer spot (leftmost), the presence of PAH is suspected. Also, any significant difference in color between the sensitizer-only spot versus sensitizer-sample spot is also considered a positive indicator for PAH.

(8) Samples which give positive results by the spot test should be submitted for GC/MS analysis to identify the source of the fluorescence.

Detection Limit and Sample Analysis

In order to determine the level of detection attainable with the equipment available, a set of standards were prepared and tested. Phenanthrene and benzo[a]-pyrene were chosen as the test standards. Phenanthrene and benzo[a] pyrene were chosen because both are considered representative of the PAH likely to occur in combustion effluent samples.

Their differences in structure may also cause differences in their detectability by the PAH spot test. Additionally, the range of aromatic fused ring compounds detectable by GC/MS is covered by these two compounds and the presence of benzo[a] pyrene, because of its carcinogenicity, must be detectable by the spot test at low concentrations.

The levels of standards prepared and the results of the analyses are presented in Table 7.8. The limit of detection of the spot test is extrapolated to be approximately 100 pg for these two materials. That is, a 1 μl sample containing 100 pg of PAH is easily detected. This observation differs by an order of magnitude from the detection limit of 10 pg previously reported (53).

Table 7.8: Results of Spot Test Analysis of Standards

...... Phenanthrene		..... Benzo[a] pyrene	
Amount	**Test Results**	**Amount**	**Test Results**
80 ng	Positive	490 ng	Positive
8 ng	Positive	49 ng	Positive
160 pg	Positive	147 pg	Positive
80 pg	Negative	98 pg	Negative
		49 pg	Negative

Source: EPA-600/7-79-207

The difference in the reported detection limit is probably due to the point at which the investigator decides to declare a significantly distinguishable difference in the fluorescent intensity of the sensitizer alone versus the sensitizer-sample spot. Since this decision is subjective, it was decided to choose a level that was easily discernable by personnel not familiar with the test.

A lower detection limit is achievable, but it would require the operator to make judgements based on subtleties of intensity and hue and would require extensive operator training and experience.

Another factor which must be taken into consideration when detection limits are compared is the ultraviolet lamp intensity. Any difference in lamp intensity will result in a difference of fluorescence intensity and, consequently, the detectable difference between the sensitizer-only and the sensitizer-sample spots would be concommitantly effected.

It is an accepted fact that lamp intensity varies with age and it is not unusual to encounter significant differences in lamp intensities in an apparatus such as the Chromatovue C-70. Differences in lamp intensity as a source of variation of the detection limit was not investigated as a part of this task.

Results

A series of industrial samples which gave negative results for both the PAH spot test and GC/MS analysis were spiked with a known amount of benzo[a]pyrene (100 pg/μl) and retested by the spot test. As expected, the samples after spiking yielded a positive indication by the PAH spot test.

Over twenty samples from industrial sites have been tested by both GC/MS and the fluorescence spot test. A partial lisitng of these samples and their results are given in Table 7.9.

Table 7.9: Results of Spot Test Analysis of Samples from Industrial Sites

Sample	Spot Test	GC/MS
. . . . Coke Oven Extracts		
A	Positive	Positive
B	Positive	Positive
. . Combustion Effluent Samples (Commercial Oil Burner). .		
A	Negative	Negative
B	Positive	Positive
C	Positive	Positive
. . Combustion Effluent Samples (Coal Fired Power Plant). .		
A	Negative	Negative
B	Negative	Negative
C	Positive	Negative
D	Negative	Negative
E	Negative	Negative
F	Negative	Negative
G	Negative	Negative
H	Positive	Negative

Source: EPA-600/7-79-207

Approximately 10% of the samples which gave a positive result of the spot test showed no PAH by GC/MS. As is illustrated, the spot test has a level of detection which is lower than that of GC/MS when the GC/MS is used in the traditional scanning mode. Taking this fact into consideration, it is not unreasonable to expect a small percentage of the samples to prove positive by the spot test and negative by GC/MS. But what is more important, is the fact that in all cases where the spot test gave negative results, the GC/MS also found no PAH. That is, no false negatives were encountered.

PORTABLE FLUOROMETRIC MONITOR TO DETECT PNA

The information in this section is based on:

> *Portable Fluorometric Monitor to Detect Polynuclear Aromatic Hydrocarbon Contamination of Work Area Surfaces,* NTIS CONF-790855-2, 1979, prepared by D.D Schuresko of Oak Ridge National Laboratory for the U.S. Department of Energy.

The need for instrumentation to monitor PNA buildup on workplace surfaces as, for example, results from aerosol condensation, has also been recognized (54)(55). Such instrumentation must be capable of: (a) functioning during actual plant operation in varied working environments; (b) detecting material spilled on different work surfaces, including machinery, plumbing, construction materials and on personnel and clothing; and (c) being easily and reliably operated by all plant personnel.

The fluorescence spotter described by D.D. Schuresko (U.S. Patent applied for) has these capabilities. This instrument, which consists of a hand-held optics unit connected via an umbilical cable to an electronics module, enables remote monitoring of work area surfaces at distances $\leqslant$1 m. The electronics module, which normally operates with ac power can also be operated on rechargeable batteries; thus the entire instrument plus battery pack is portable.

It is anticipated that portable fluorescence spotters will be used extensively to detect surface contamination in changing areas, lunchrooms, shops, control rooms and other "clean" areas in coal conversion facilities, and to monitor skin contamination of coal plant workers. The currently used method of detecting contamination is to turn off ambient lighting and scan the suspected area with a black light.

In contrast, the newly developed spotter (a) can be operated outdoors in direct sunlight or indoors in the presence of strong background illumination; (b) provides a quantitative measure of the amount of fluorescent material; (c) will discriminate between the fluorescence of organic materials and some inorganic compounds based on their fluorescence lifetimes; and (d) does not present a vision hazard to personnel.

The spotter induces and detects the fluorescence of PNA that characteristically absorb light in the 350 to 440 nm region of the spectrum and fluoresce with high efficiency in the blue-green region of the spectrum. Multiring heteroatom aromatic compounds, including acridines, are also detected, although they generally absorb light and fluoresce at longer wavelengths than do their pure hydrocarbon counterparts.

The spotter has been laboratory tested with pure compounds and with several coal and oil shale products and wastes. When operated in a laboratory area illuminated by fluorescent lighting, the spotter can typically detect 0.1 μg of perylene (as a dilute solution in cyclohexane) located 50 cm distant. Considering that 10 μg doses of several PNA will induce changes in the metabolism of cultured mammalian cells (56)(57), it is evident that the high sensitivity of the spotter is appropriate to its intended task.

ECT PNA

ynuclear Aromatic
urfaces, NTIS CONF-
of Oak Ridge
t of Energy.

lup on workplace surfaces
has also been recognized
: (a) functioning during
nts; (b) detecting material
ery, plumbing, construction
ing easily and reliably

sko (U.S. Patent applied for)
ists of a hand-held optics
nics module, enables remote
n. The electronics module,
operated on rechargeable
ack is portable.

will be used extensively to
chrooms, shops, control
acilities, and to monitor skin
ly used method of detecting
scan the suspected area with

e operated outdoors in direct
round illumination; (b) pro-
rescent material; (c) will
naterials and some inorganic
and (d) does not present a

f PNA that characteristically
pectrum and fluoresce with
ctrum. Multiring heteroatom
detected, although they gen-
gths than do their pure hydro-

compounds and with several
erated in a laboratory area
n typically detect 0.1 μg of
ated 50 cm distant. Consider-
changes in the metabolism of
hat the high sensitivity of the

In this regard, the spotter might prove to be particularly useful in quantitatively measuring PNA skin contamination caused by contact with coal-derived liquids, thus providing accurate data for correlation with the incidence of skin lesions.

REFERENCES

(1) Schaad, R., *Chromatography Reviews,* 13, 61 (1970).
(2) Cook, J.W., Hewett, C.L. and Heiger, I., *J. Chem. Soc.,* 395 (1933).
(3) Cook, J.W. and Hewett, C.L., *J. Chem. Soc.,* 398 (1933).
(4) La Budde, J.A. and Heidelberger, C.J., *JACS,* 80, 1225 (1958).
(5) Berenblum, I. and Schoenthal, R., *Cancer Research,* 6, 699 (1946).
(6) Cook, J.W., Ludwiczak, R.S. and Schoenthal, R., *J. Chem. Soc.,* 1112 (1950).
(7) Hood, L.V. and Winefordner, J.D., *Anal. Chim. Acta,* 42, 199 (1968).
(8) Sawicki, E., Corey, R.C., Dooley, A.E., Gisclard, J.B., Monkman, J.L., Neligan, J.B. and Ripperton, L.P., *Health Lab. Sci.,* 7, 56, 60, 68 (1970).
(9) Matsushita, H., Esumi, Y. and Yamada, K., *Bunseki Kagaku,* 19, 951 (1970).
(10) Sawicki, E., *Talanta,* 16, 1231 (1969).
(11) Wehry, E.L., Mamantov, G., Kemmerer, R.R., Stroupe, R.C., Tokousbalides, P.T., Hinton, E.R., Hembree, D.M., Dickinson, R.B, Jr., Garrison, A.A., Bilotta, P.V. and Gore, R.R., *Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons,* pp. 193-202, P.W. Jones and R.I. Freudenthal (editors), Raven Press, New York, NY (1978).
(12) VoDinh, T., *Anal. Chem.,* 50, 396 (1978).
(13) Sawicki, E., Stanley, T.W. and Elbert, W.C., *J. Chromatog.,* 20, 348 (1965).
(14) Sawicki, E., Corey, R.C., Dooley, A.E., Gisclard, J.B., Monkman, J.L., Neligan, R.E. and Ripperton, L.A., *Health Lab. Sci.,* 7, Supplement 3, 31 (1970).
(15) Searl, T.D., Cassidy, F.J., King, W.H. and Brown, R.A., *Anal. Chem.,* 42, 954 (1970).
(16) *Ultraviolet Atlas of Organic Compounds,* 5 Vols., Plenum Press, New York, NY (1967-1968).
(17) Ungnade, H.E. (editor), *Organic Electronic Spectral Data,* Interscience Publishers, Inc., New York, NY (1960-present).
(18) Wilmhurst, S.R., *J. Chromatog.,* 17, 50 (1965).
(19) Deamio, L. and Corn, M., *Anal. Chem.,* 38, 131 (1966).
(20) Golay, J.J.E., *Theory and Practice of Gas Liquid Partition Chromatography with Coated Capillaries in Gas Chromatography,* V.J. Coates, H.J. Noebels and I.S. Fagerson (editors), Academic Press, New York, NY (1958).
(21) Lee, M.L., Vassilaros, D.L., White, C.M. and Novotny, M., *Anal. Chem.,* 51, 768 (1979).
(22) Janini, G.M., Johnston, K. and Zielinski, W.L., Jr., *Anal. Chem.,* 47, 670 (1975).
(23) Oi, W. and Inabe, E., *Yakugaku Zasshi,* 87, 741 (1967).
(24) Marmon, D.M., *J. Ass. Off. Analytical Chem.,* 57, 495 (1974).
(25) Nagy, F. and Sohar, J., *Chem. Zvesti,* 16, 389 (1962).
(26) Martrka, M., Kroupa, J. and Spevak, A., *Coll. CS. Chem. Commun.,* 36, 1379 (1971).
(27) Lao, R.C., Thomas, R.S. and Monkman, J.L., "Chemistry, Metabolism, and Carcinogenesis," *Carcinogenesis: A Comprehensive Survey, Vol. 1: Polynuclear Aromatic Hydrocarbons,* R. Freudenthal and P.W. Jones (editors), Raven Press, NY (1976).
(28) Fox, M.A. and Staley, S.W., *Anal. Chem.,* 48, 992 (1976).
(29) Dong, M., Locke, D.C. and Ferrand, E., *Anal. Chem.,* 48, 368 (1976).
(30) Klimisch, H.J., *Anal. Chem.,* 45, 1960 (1973).
(31) Zielinski, W.L., Jr., Johnston, K. and Muschik, G.M., *Anal. Chem.,* 48, 907 (1976).
(32) Janini, G.M., Muschik, G.M. and Zielinski, W.L, Jr., *Anal. Chem.,* 48, 809 (1976).
(33) Janini, G.M., Muschik, G.M., Schroer, J.A. and Zielinski, W.L., Jr., *Anal. Chem.,* 48, 1879 (1976).
(34) *GC Reporter,* 2(2), 4 (1977).
(35) Supelco, Inc., *Supelco Technical Bulletin,* 773, Bellefonte, Penn. (1977).
(36) Barrall, E.M., II and Johnson, J.F., *Liquid Crystals and Plastic Crystals, Vol. 2,* G.W. Gray and P.A. Winsor (editors), John Wiley & Sons, Inc., (1974).

(37) Janini, G.M., Shaikh, B. and Zielinski, W.L., Jr., *J. Chromatog.,* 132, 136 (1977).

(38) Robertson, D.J., Elwood, J.H. and Groth, R.H., *Chemical Composition of Exhaust Particles from Gas Turbine Engines.* Final report prepared by United Technologies Corporation, East Hartford, Conn., under Contract No. 68-02-2450 to the U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/2-79-041 (February 1979).

(39) Braddock, J.N. and Gabele, P.A., "Emissions Patterns of Diesel-Powered Passenger Cars–Part II," SAE Paper No. 770168, Detroit, MI (February 1977).

(40) Hare, C.T. and Bradow, R.L., "Characterization of Heavy-Duty Diesel Gaseous and Particulate Emissions, and Effects of Fuel Composition," SAE Paper No. 790490, Detroit, MI (February 1979).

(41) Hare, C.T. and Baines, T.M., "Characterization of Particulate and Gaseous Emissions from Two Diesel Automobiles as a Function of Fuel and Driving Cycle," SAE Paper No. 790424, Detroit, MI (February 1979).

(42) Matsushita, H., Esumi, Y. and Suzuki, A., "Analysis of Polynuclear Hydrocarbons in Petroleum," *Bunseki Kagaku,* 21(3):331-7 (1972).

(43) Uthe, J.F., Reinker, J. and Gesser, H.D., "Extraction of Organochlorine Pesticides from Water by Porous Polyurethane Coated with Selective Absorbent," *Environ. Letters,* 3:117 (1972).

(44) Musty, P.R. and Nickless, G., "The Extraction and Recovery of Chlorinated Insecticides and Polychlorinated Biphenyls from Water Using Porous Polyurethane Foams," *J. Chromatogra.,* 100:83 (1974).

(45) Lawrence, J. and Tosine, H.M., "Adsorption of Polychlorinated Biphenyls from Aqueous Solutions and Sewage," *Environ. Sci. Technol.,* 10:381 (1976).

(46) Acheson, M.A., Harrison, R.M., Perry, R. and Welling, R.A., "Factor Affecting the Extraction and Analysis of Polynuclear Aromatic Hydrocarbons in Water," *Water Res.,* 10:207 (1976).

(47) Sawicki, E., Stanley, T.W., Elbert, W.C., Meeker, J. and McPherson, S.P., "Comparison of Methods for the Determination of Benzo[a]pyrene in Particulates from Urban and Other Atmospheres," *Atmos. Environ.,* 1:131 (1967).

(48) Borneff, J., *Polycyclic Aromatic Hydrocarbons in Water,* Summary of the German work on PAH.

(49) World Health Organization, *International Standards for Drinking Water,* 3rd ed., Geneva (1971).

(50) Strosher, M.T. and Hodgson, G.W., "Polycyclic Aromatic Hydrocarbons in Lake Waters and Associated Sediments: Analytical Determination by Gas Chromatography-Mass Spectroscopy," *Water Quality Parameters,* ASTM-STP-573, pp. 259-270 (1975).

(51) Giger, W. and Schaffner, C., "Determination of Polycyclic Aromatic Hydrocarbons in the Environment by Glass Capillary Gas Chromatography," *Anal. Chem.,* 50, pp. 243-249 (1978).

(52) Kubota, H., Griest, W.H. and Guerin, M.R., "Determination of Carcinogens in Tobacco Smoke and Coal-Derived Samples–Trace Polynuclear Aromatic Hydrocarbons," *Trace Substances in Environmental Health,* Vol. IX, pp. 281-289, D.D. Hemphill (editor), University of Missouri, Columbia (1975).

(53) *Sensitized Fluorescence for the Detection of Polycyclic Aromatic Hydrocarbons,* EPA-600/7-78-182, NTIS No. PB 287-181 IAS (September 1978).

(54) Brookhaven National Laboratory, *Report of the Working Group on Assessing Industrial Hygiene Monitoring Needs for the Coal Conversion and Oil Shale Industries,* Otto White, Chairman (August 1978).

(55) Schuresko, D.D. and Jones, G., "A Portable Fluorometric Monitor to Detect PNA Contamination of Work Area Surfaces," *Proceedings of the Symposium on Assessing the Industrial Hygiene Monitoring Needs of the Coal Conversion and Oil Shale Industries,* Brookhaven National Laboratory (November 1978).

(56) Schuresko, D.D., et al, unpublished results.

(57) Nebert, D.W. and Gelboin, H.V., *J. Biol. Chem.* 243(23), 6242 (1968).

ADDENDUM

Laser Technique to Detect PAH

It was recently reported (U.S. Department of Energy, "Laser Technique to Help Detect Cancer-Causing Industrial Pollutants," *Energy Insider,* 3:21, October 13, 1980) that a new laser technique to identify PAH has been developed by scientists at Lawrence Livermore National Laboratory (LLNL). The system can detect concentrations as low as one part per billion in a sample containing hundreds of chemicals. This is one thousand times more sensitive than high performance liquid chromatography used alone. The system also is estimated to cost ten times less than GC/MS systems of comparable sensitivities.

LLNL is using the technique on samples of fly ash from two coal-fired power plants in the Western United States to determine why the ash from one plant showed cancer-causing potential while the ash from the other did not.

Since the ash contains hundreds of chemical compounds, it is essential to separate them to find any differences. Using this laser technique, the PAH present in the fly ash can be separated and detected.